Ground and Metastable States in γ-Ce from Correlated Band Theory

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Multiple energy minima of the LDA+U energy functional are obtained for γ-Ce when it is implemented in a full potential, rotationally invariant scheme including spin-orbit coupling, and different starting local configurations are chosen. The lowest energy solution leads to a fully spin polarized 4f state and the lattice constant of γ-Ce. The higher energy local minima (additional self-consistent solutions) are shown to be strongly indicative of crystal electric field and multiplet excitations.

The isostructural α - γ phase transition in Ce, and the character of the phases separately, have been a subject of continious theoretical efforts for decades. Experimentally, the low temperature fcc α phase of Ce transforms to the fcc γ phase at the high temperatures with a large increase of the volume. When pressure is applied, the crystal collapses back into the α phase in a first-order phase transition. The room temperature $\gamma - \alpha$ phase transition occurs at ≈ 7 kbar pressure with the decrease of the volume of $\approx 15\%$.

Several theoretical models have been suggested and they are described in some detail in Ref. [1]. The difference between the models arises from the different treatments for the Ce 4f electrons. The promotional model [2] assumed depopulation of the 4f level upon compression, but does not agree with the results of various experiments which indicate little change in the 4f occupation. Band structure calculations also indicate that promotion is too high in energy to drive the transition, and the 4f occupation remains near unity. [3] The Mott transition model [4] assumes the transformation of localized to band-like 4f state with the decrease of volume and is similar to the Mott-Hubbard metal-insulator transition. First principles calculations using the self interaction correction (SIC) to the LDA [5] produce total energy minima for localized (γ) and band (α) states with formally the same SIC total energy variational functional, and are in accord with the Mott transition model. However, the use of atomic sphere approximation (ASA), which sphericalizes the potential and density within large atomic spheres, limits the ability of these calculations to produce quantitative total energy description of the system with highly non-spherically symmetric 4f electron charge/spin densities.

The other viable theoretical model is the Kondo volume collapse (KVC) model [6]. The essence of the KVC is an assumption of localized f states in the both α and γ phases of Ce. The α phase consists of a mixed valence 4f state while the γ phase has almost integer 4f occupancy. The phase transition is due to the entropy contribution of the localized 4f state. The relation between KVC and Mott transition model was analyzed recently in Ref. [1] and quantitative arguments in favor of KVC model were provided.

The local (spin) density approximation (LDA) has had tremendous success in the quantitative description of a wide variety of solids, [7] but the rare earths are extreme cases where the LDA description is inadequate. The "correlated band theory" (LDA+U) approach has had much success in the treatment of correlated magnetic insulators where LDA results are incorrect. In this paper we explore not the $\gamma - \alpha$ transition *per se*, but the γ phase itself, by an application of the LDA+U approach that includes the new features (1) a full potential method is used, which enables the novel features we uncover, and (2) the LDA+U method is applied to a metal where the interaction of the local orbitals with the conduction states is a central part of the physics. For the first time, multiple LDA+U energy minima (ground plus metastable states) are obtained within a specified broken symmetry, and we discuss how the various states are related to 4f excitations in the γ phase.

The LDA+U method [8] is based on an energy which is a functional of the spin densities $\{\rho^s, s = \pm 1\}$, and the occupation matrices $\{n^s_{m,m'}\}$ of the 4f orbitals labelled by their azimuthal projections $m \equiv m_\ell$. There is every reason to expect that, within the allowed values of ρ^s and n^s, there can be local energy minima as well as the absolute minimum, which represents the ground state energy of the system. (Such local minima are rarely found within LDA except in magnetic systems.) The formal meaning of these local minima, as well as the formal underpinnings of the LDA+U approach itself, remain to be settled, but – like the Kohn-Sham eigenvalues (the band structure) which have little formal meaning but immense practical importance – these minima will be shown to bear a close relationship to local excitations of the 4f shell.

Our results are based upon the full-potential linearized augmented plane wave method (LAPW) [9] as the basis for total energy calculations with the rotationally invariant LDA+U functional [10], with spin-orbit coupling (SOC) is included self-consistently [11]. Literature values [12] are used for the on-site repulsion $U = 6.1$ eV and exchange $J = 0.7$ eV (Slater integrals, $F_0 = 6.10$ eV, $F_2 = 8.34$ eV, $F_4 = 5.57$ eV, $F_6 = 4.12$ eV). Ferromagnetic spin alignment is assumed (allowed, not imposed) since local moments are present in paramagnetic high temperature γ phase of Ce [13].

The key to finding the various solutions (local minima) is to start from atomic densities and different 'guesses' for the 4f occupation matrices n^s and then obtain self-consistently both spin/charge densities and occupation matrices. As an intuitive guess for 4f occupations we use the fully spin-polarized state (Tr $n^{\uparrow}$=1, Tr $n^{\downarrow}$=0) and choose various orbital characters for $n^{\uparrow}_{m,m'}$.

Ground State. The calculated equilibrium lattice constant (cf. Table I) is very close to the experimental value of γ-Ce at zero pressure and room temperature [14]. The calculated bulk modulus is about 25% larger than the experimental value, similar to other calculations that have treated the localized character of the 4f state in γ-Ce.

For the γ phase volume (lattice constant a=9.76 a.u.) we find the lowest solution to be fully spin polarized with the f occupation of 1.04. This state is primarily m_l=-2 ($m_j = -\frac{3}{2}$), with some mixing in of the spin-majority $m_l = 2$ state. The LDA+U yields significant enhancement for the absolute values of both spin and orbital magnetic moments (anti-aligned in accord with the 3rd Hund's rule) in comparison with LDA results.

The electronic density of states for the γ-Ce ground state is shown in Fig. 1 in comparison with the result of relativistic (with SOC) LDA calculations. The f-majority peak at the bottom of valence band ($\approx$ 2.5 eV below the Fermi level) indicates the position of the localized 4f state, in quantitative agreement with the resonant photoemission measurements [15]. The difference between LDA+U and LDA is due to the localization of the 4f state, which removes both majority and minority 4f states from the vicinity of the Fermi level. Since the 4f state is not well separated from the valence band (cf. Fig. 1) we conclude that in spite of its localized character the 4f state in γ-Ce cannot be treated as core-like.

Metastable States. As mentioned above, several self-consistent solutions corresponding to different (local) minima of the LDA+U energy functional are possible. Different minima must be searched for by exploring various regions of the underlying space. Our initial starting points consisted of fully spin polarized $4f^1$ with different orbital characters $\{m_l\}$. Our initial and final (self-consistent) majority spin occupation matrix elements are shown in Table II. In the LDA+U calculations the spin polarization enters as an effective magnetic field providing the spin quantization axis and the direction of the quantization axis is chosen along z([001]).

The LDA+U minima can be considered as mean-field-like projections (in the Fock space) of many-body wavefunctions on the single-particle angular basis set. The interpretation is much simpler for an f^1 ion than it would be for a multi-electron ion because the $\{m_l, m_s\}$ and $\{J, J_z\}$ representations are unitarily related. In the simple crystal-electric-field (CEF) model for the paramagnetic Ce^{3+} ion [17] the ground state is formed by one of the Γ_7 and $\Gamma_8^{1,2}$ doublets from $J = 5/2$ multiplet [16]. In order to compare the CEF model [17] with the LDA+U results, we apply to the LDA+U solutions the unitary transformation from $\{m_l, m_s\}$ representation to $\{J, J_z\}$ representation with $J = 5/2, 7/2$. The states from Table III are then classified as follows:
Solution (1) - Ground State: It has 96% $m_l = -2$, with 3% $m_l = 2$ mixed in. The transformation to $\{J, J_z\}$ representation yields 69% of $|5/2, -3/2>$ and 1% of $|5/2, 5/2>$ states from $J = 5/2$ multiplet, plus 27% of $|7/2, -3/2>$ and 3% of $|7/2, 5/2>$ states from $J = 7/2$. We conclude that the *Solution 1* consists of 70% states from the $J = 5/2$ multiplet which are the linear combination of the CEF levels Γ_7 and Γ_8^1, and 30% states from the $J = 7/2$ multiplet.
Solution (2): Roughly equal amounts of $m_l = -3$ and $m_l = +1$) in this solution indicates coupled $m_j = -5/2$ and $m_j = 3/2$ states. It consists of 55% states from $J = 5/2$ multiplet (combinations of the CEF levels Γ_7 and Γ_8^1) and 45% of states from $J = 7/2$.
Solution (3), involving admixture of $m_l = -1$ with 25% $m_l = +3$, which transforms to an admixture of 42% of $|5/2, -1/2>$ ($|\Gamma_8^2>$) state with the 58% of $|7/2, 7/2>$.
Solution (4), pure $m_l = 0$, corresponds to the combination of 42% of $|5/2, 1/2>$ ($|\Gamma_8^2>$) state with the 58% of $|7/2, 1/2>$, and lies 232 meV above the ground state.

These correlated band structure calculations are producing metastable solutions that contain the CEF states from the conventionally presumed lowest multiplet for Ce^{3+}. In addition, there is a considerable fraction of the states from the first excited $J_{7/2}$ multiplet that must be understood.

There are two important reasons why our solutions do not correspond directly to CEF levels as normally considered. First, the CEF picture assumes ideal cubic symmetry, whereas a 4f state in γ-Ce is actually surrounded by twelve atoms whose own moments are oriented randomly, hence breaking cubic symmetry. In addition the non-cubic nature of the 4f density perturbes the conduction electron density, which leads to a non-cubic local field. Secondly, in our calculations we have artificially ordered the spins of the magnetic ions and allowed orbital moments, which reduces out site symmetry to tetragonal.

The comparison between LDA+U calculated splitting scheme with the results of inelastic neutron scattering experiments [19] is shown in Fig. 2. It is clearly seen that *Solutions 1-3* lie well within the range of low-energy excitations peak and reflect the mixed CEF and spin-orbit excitations. The energy position of *Solution 4* (232 meV) agrees quantitatively with the experimental inelastic peak at 260 meV. This peak is usually interpreted as the spin-orbit excitation $^2F_{5/2} \rightarrow {}^2F_{7/2}$ [19]. Our calculations suggest that this interpretation is oversimplified since the states from both lower $^2F_{5/2}$ and first excited $^2F_{7/2}$ multiplets are mixed in the ground and excited states of γ-Ce. The spectrum from present LDA+U calculations are in better agreement with the experiment

[19] than previously reported results of SIC calculations [20] (86-100 meV and 130 meV).

In order to classify the LDA+U solutions we transform them from the compex to the cubic spherical harmonics. *Solution (1)* involves admixture of xyz and $(x^2-y^2)z$ states; *Solutions (2) and (3)* consist of mixed $(x^2-z^2)y$ and $(y^2-z^2)x$ states; and *Solution (4)* has $(5z^2-3r^2)z$ symmetry. All the LDA+U solutions have the tetragonal symmetry assumed in the calculations. The localized states without SOC are formed by CEF states in $\{L, L_z\}$ representation and for $L=3$ these are $\Gamma_2, \Gamma_4, \Gamma_5$ states [21]. In fully spin-polarized case the spin-orbit coupling $\xi(\vec{l}\cdot\vec{s})$ is reduced to $\xi(\hat{l}_z\hat{s}_z)$ and the eigenvalues of localized "CEF+SOC" model Hamiltonian are easily obtained. The "CEF+SOC" coupling scheme is presented in Fig. 3 and shows how the LDA+U solutions result from CEF eigenstates coupled by spin-orbit coupling. From the total energy differences between LDA+U solutions we then derive the CEF splitting parameters $\Delta_{2,5} = \Gamma_2 - \Gamma_5 = 90$ meV and $\Delta_{4,2} = \Gamma_4 - \Gamma_2 = 107$ meV and SOC parameter ξ of 66 meV (SOC splitting $= (7/2)\xi = 231$ meV).

The scheme in Fig. 3 allows more eigenstates than the calculated local minima of the LDA+U total energy functional. In each case the occupation matrices $n_{m_l,m_l'}$ for these additional states have the non-zero elements in the same $\{m_l, m_l'\}$ sub-space as one of the metastable states. As a result the minimization procedure yields the lowest total energy state in given $\{m_l, m_l'\}$ sub-space and the higher states do not appear among variational LDA+U solutions.

The physical origin of the CEF splitting can be understood to be due to the anisotropy of the mixing interaction between conduction band and localized f-states [22]. We obtain the CEF splitting for γ-Ce of the order of 100 meV comparable with the SOC splitting of 231 meV. In both ground and excited states the CEF levels are then mixed by SOC yielding low-energy excitations of the order of 20-50 meV and high-energy excitations about 230 meV.

The results of LDA+U calculations allow us to conclude that the interaction between conduction band and localized f-states plays an important role for the both ground and excited states in $\gamma-$Ce. As a result, the Ce f-states are *not core-like* and should be treated in terms of quantum impurity (Anderson) model [25] rather than as localized states of Ce^{3+} ion in the cubic CEF. The present LDA+U calculations correspond to the numerical solution of the lattice Anderson model in static mean-field approximation with the assumed ferromagnetic order. This simplification does not allow us to describe quantitatively the paramagnetic (disordered local moment) high-temperature state of $\gamma-$Ce observed experimentally. The treatment of this paramagnetic state requires the use of dynamic mean-field parametrization for the self-energy [26].

Recently, Solovyev *et al.* [23] proposed a correction to the LDA+U total energy functional [24] when SOC is included and non-collinear magnetic configurations are considered. This correction accounts for additional contributions to the exchange energy due to non-zero spin-off-diagonal elements of the occupation matrix $\{n^{s,-s}_{m,m'}\}$. We performed LDA+U calculations with this spin-off-diagonal correction [23] and found that the spin-off-diagonal occupations are very small and have minute effects on the values of spin and orbital magnetic moments, and the total energies (less than 2 meV) for ground and metastable states (cf. Table II) in $\gamma-$Ce.

To summarize, we have obtained the ground and three metastable states from relativistic (with spin-orbit coupling) spin-polarized full-potential LDA+U calculations for fcc Ce. The ground state has equilibrium lattice constant of γ-Ce. Our calculations reproduce the localized character of 4f states in γ-Ce, which however cannot be treated as a part of atomic core. Analysis of various LDA+U solutions allows us to make a comparison between correlated band theory results and CEF model. The excitation energies calculated from the total energy differences between LDA+U solutions are in reasonable agreement with the experimental data.

We are grateful to D. L. Cox for helpful comments. This research was supported by National Science Foundation Grant DMR-9802076, and by NSF Grant PHY-94-07194 while A.I.L and W.E.P. were in residence at the Institute of Theoretical Physics, UCSB.

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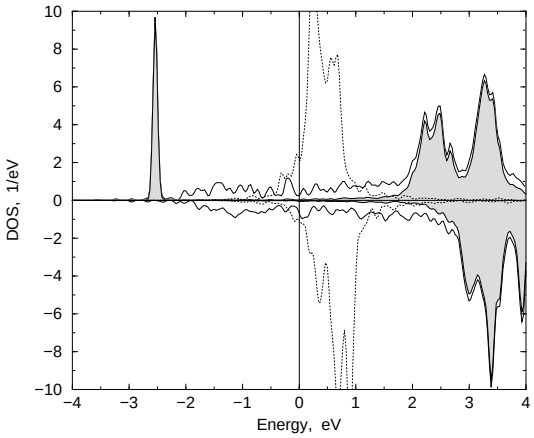

FIG. 1. Spin-resolved total and partial 4f densities of states for ordered γ-Ce. Majority are plotted upwards, minority downwards. The 4f partial DOS from LDA is dotted. The full line gives the LDA+U DOS, with the 4f contribution filled in. The 4f DOS peaks near the Fermi level in both spins are well removed from the Fermi level by LDA+U.

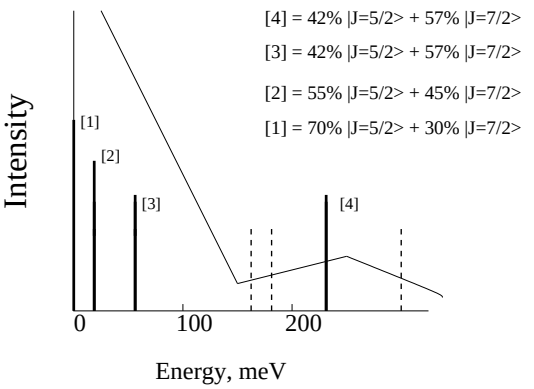

FIG. 2. Schematic sketch of the experimental inelastic neutron scattering intensity in comparison with the energy positions of LDA+U calculated ground and excited states [1]-[4]. Additional inferred localized excitations are shown (dotted lines).

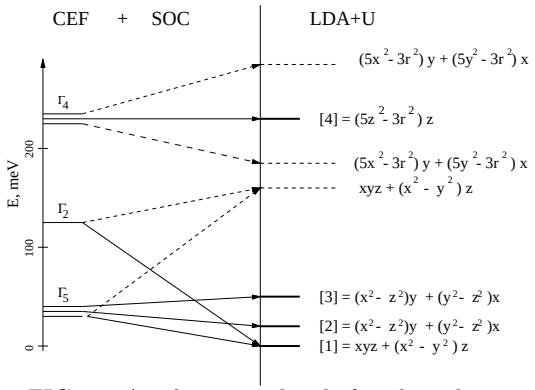

FIG. 3. A schematic sketch for the relation of the CEF levels to the LDA+U calculated ground and excited states [1]-[4] (full lines). Additional possible localized excitations are shown (dotted lines).

TABLE I. The equilibrium lattice constant $(a, a.u.)$ and bulk moduli $(B, kbar)$ as a result of LDA+U calculations.

	LAPW	LMTO-ASA [5]	LMTO-ASA [18]		Exp. [5]
	LDA+U	SIC	f-core LDA	f-core GGA	
a	9.83	9.58	9.69	10.02	9.76
B	296	310	312	288	210, 244

TABLE II. The elements of the occupation matrix $n_{m,m'}$ (spin - majority) (initial assignment n^0 and self-consistent n^{scf}); spin $(2 < S_z >)$, orbital $(< L_z >)$ moments and the total energy increase with respect to the ground state $(\Delta E, meV)$ for different LDA+U self-consistent solutions in the order of increasing total energy. The only those elements of occupation matrix which are bigger than 0.01 are shown. The spin-minority occupation matrix is almost zero since there is a complete spin-polarization of the 4f-shell.

$n^0_{m,m'}$			$n^{scf}_{m,m'}$			$2 < S_z >$	$< L_z >$	ΔE
Solution 1								
m,m'	-2	2	m,m'	-2	2	1.18	-1.87	0
-2	1	0	-2	0.960	0.143			
2	0	0	2	0.143	0.030			
Solution 2								
m,m'	-3	1	m,m'	-3	1	1.18	-0.75	19
-3	1	0	-3	0.438	-0.484			
1	0	0	1	-0.484	0.552			
Solution 3								
m,m'	-1	3	m,m'	-1	3	1.18	0.001	52
-1	1	0	-1	0.737	-0.423			
3	0	0	3	-0.423	0.253			
Solution 4								
m,m'	0		m,m'	0		1.14	-0.004	232
0	1		0	0.979				